Synthesis & Characterization of Lanthanum Copper Titanium Dioxide ($La_{2/3}Cu_3Ti_4O_{12}$) Ceramics by Conventional & Microwave Processing Routes

A thesis submitted in partial fulfillment of the requirement

For the degree of

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IN

PHYSICS

By

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National Institute of Technology, Rourkela

CERTIFICATE

This is to certify that the thesis entitled "**Synthesis & Characterization of Lanthanum Copper Titanium Dioxide ($La_{2/3}Cu_3Ti_4O_{12}$) Ceramics by Conventional & Microwave Processing Routes"** submitted by Miss Surya Mallick in partial fulfillment for the requirement for the award of degree of Master of Science degree in Physics at National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance in Electro ceramic Lab of Department of Physics.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or Diploma.

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ACKNOWLEDGEMENT

On the submission of my thesis report titled "**Synthesis & Characterization of Lanthanum Copper Titanium Dioxide ($La_{2/3}Cu_3Ti_4O_{12}$) Ceramics by Conventional & Microwave Processing Routes",** I would like to convey my gratitude and sincere thanks to my supervisor Prof. Pawan Kumar, Department of Physics for his constant motivation and support during the course of my work in the last one year. I truly appreciate and value his esteemed guidance and encouragement from beginning to the end of this thesis. I am indebted to him for having helped me, shape the problem and providing insights towards the solution.

I am also thankful to all the PhD and M. Tech(R) scholars in the Electro Ceramic lab for their liberal co-operation with extending their all analytical facilities.

Dedicated to my parents

Abstract

LCTO has been prepared using conventional synthesis method and microwave synthesis method. Sintering has been done at 1000^0C for 4 hours in conventional way and in a microwave way for 20, 30, 60 minutes. Density measurement, XRD analysis, dielectric constant and dielectric loss measurement, SEM measurement has been done. Highest density achieved in microwave sintered sample. XRD confirmed perovskite cubic structure. Dielectric measurement was done in the frequency range 1 kHz to 1 MHz.

CONTENT

Chapter 4

Chapter 1

1.1 Introduction

1.1.1 Dielectric Materials and high Dielectric constant materials

A dielectric is a non-conducting substance used to describe materials where the dielectric polarization is important. It support charge without conducting. In principle all insulators can be dielectric but all dielectric cannot be insulator. The dielectric constant of a material provides a measure of its effect on a capacitor. The ratio of the capacitance of a capacitor containing the dielectric to that of an identical but empty capacitor given by $\varepsilon_r = C/ C_0$, where ε_r = dielectric constant, C = capacitance in presence of dielectric and and C_0 in vacuum. CCTO shows an extremely high dielectric constant which is contrast to ferroelectrics like $BaTiO_3$ is nearly constant in a broad temperature range. Thus this material has attracted tremendous attention due to possible application eg for enhancing the performance of capacitive electronic elements. Numerous investigations have revealed that the dielectric properties of CCTO strongly depend on the processing conditions during preparation, the type of external contacts and the measuring frequency. CCTO showed the highest dielectric constant of all investigated compounds. However, as mentioned above, the absolute values of the CDCs in CCTO are strongly dependent on various factors, like processing conditions during sample preparation and frequency. Thus measurements at a single frequency in one polycrystalline sample may not be sufficient to exclude the occurrence of CDCs in other

materials and it may be possible to find similarly spectacular dielectric properties also in other CCTO-related compounds.

1.1.2 Literature survey

Ferroelectric ceramics are important electronic materials that have a wide range of industrial and commercial applications, such as high-dielectric constant capacitors, piezoelectric sonar or ultrasonic transducers, pyro electric , medical ,and ultrasonic motors, to name a few. The performances of ferroelectrics are closely related to the ways they are processed. The conventional solid state reaction method requires high calcination and sintering temperatures, resulting in the loss of lead, bismuth or lithium components due to their high volatilities, thus worsening the microstructural and subsequently the electrical properties of the ferroelectric materials. Various wet chemistry based routes have been developed to synthesize ultra-fine and even nano-sized ferroelectric powders. However, most of the chemistry based routes still involve calcinations, although at relatively lower temperatures. High energy mechanochemical milling process has been shown that some ferroelectric materials can be synthesized directly from their oxide precursors in the form of nano-sized powders, without the need for the calcination at intermediate temperatures, thus making the process very simple and cost-effective. A large number of ferroelectric materials, including lead-containing ferroelectrics, antiferroelectrics and relaxors, and bismuth-containing Aurivillius families, have been synthesized by the high-energy milling process. Some ferroelectrics, such as barium titanate ($BaTiO_3$ or BT), lead iron tungstate [$Pb(Fe_{2/3}W_{1/3})O_3$ or PFW], and several bismuth having materials, which is not directly produced from their mixture of oxide formed at relatively low temperature after their precursors are

activated by an high-energy milling. This review presents an overview of the recent progress in the synthesis of ferroelectric ceramic powders using various high-energy milling techniques [1,2]

CCTO is a well-known non-ferroelectric material possessing high and nearly constant (room temperature to (300^0C) dielectric constant at 1kHz.Its being widely used in the electronic industries to manufacture electronic components such as multilayer capacitor (MLCC), DRAMs, microwave devices, electronic devices in automobiles and aircrafts. The property like permittivity of CCTO depends upon the size of the particle and morphology of powder. The particle size and powder morphology of CCTO depend on different processing parameters that are temperature, heating rate, duration and atmosphere. These ceramics are sintered at low temperature nearly 1050^0C, present original dielectric properties. The relative permittivity is in the temperature range ($-150<T<250^0$C) is significantly higher than the one reported in theory. Moreover the copper oxide phase beside the perovskite CCTO plays important role for enhancing dielectric properties.

Chapter 2

2.1 Experimental Procedure

Precursors La_2O_3, CuO and TiO_2 were taken in stoichiometric proportion for preparation of $La_{2/3}Cu_3Ti_4O_{12}$ (LCTO). Starting raw materials were measured using the high precision balance machine. These precursors were together ball milled for 6 hours using zirconia balls (powder to balls ratio 1:3) in acetone as medium. Then the mixture was thoroughly grounded in agate mortar for1 hour. After that the calcinations is performed in a high temperature furnace at 1000˚C, for 4, 6 and 8 hours respectively. Phase formation was confirmed through X-ray powder diffraction study. The XRD patterns of the calcined samples were taken at an angle from 20 to 70 degree with a scanning rate of 2 degree per minute.

2.1.2 Synthesis Process

For the preparation of 20 grams of $La_{2/3}Cu_3Ti_4O_{12}$, the amount of the raw materials taken as follows.

SAMPLE	MOLECULAR WEIGHT	QUANTITY USED
La_2O_3	325.81	2.4429
CuO	79.545	5.3679
TiO_2	79.9	7.1891

These raw materials were mixed thoroughly using ball milling technique and then grinded in the agate mortar for nearly 1 hour so as to form complete mixture of the starting raw powder.

2.1.2 Calcination

After synthesis the powdered sample is heated or calcined in a furnace for 4, 6 and 8 hours at temperatures 1000 ℃ at a heating rate of 5 ℃ per minute. During the calcination process ferroelectric phase is obtained as a result of solid phase reaction between the constituents. The calcination temperature is very much important because it affects the electrical and mechanical properties of the ceramics to a large extent. The homogeneity and the density of the resultant ceramic ultimately depends upon the calcinations conditions. This also affects the electromechanical properties of the ceramic product.

2.1.3 Binder Addition

Binders serve as adhesive among the powder particles which give mechanical strength to the green body. In the present study 2wt% poly vinyl alcohol (PVA) was mixed in the calcined powder sample as binder. Since (PVA) is an organic binder it vaporizes in the early stage of sintering. The binder must provide the desired rheological properties to feed material so that the powder can be consolidated into the desired shape and then must be removed completely from the shaped powder during firing, without the disruption of the particle packing or any chemical reaction with the powder.

2.1.4 Sintering

Cylindrical shaped pallets were taken for sintering. In our experiment we have done sintering using two different methods one is conventional sintering and other one is microwave sintering method. In conventional sintering process raw powder mixture was fired at 1000 ^{0}C for 4 hours whereas in microwave sintering process raw powder mixture was fired at 1000 ^{0}C for 20,40 and 60 minutes. Microwave sintering has advantages over conventional heating like (i) fast heating, (ii) volumetric heating, (iii) less energy consumption. So microwave sintering produce uniform and dense grain morphology.

2.1.5 Electroding

A layer of metallic silver in paste form is applied on the plane surface of the sintered pallets of LCTO samples. Ideally, the silver should adhere strongly to the ceramic, it should be very thin, practically zero resistance, and with a good chemical and physical durability. The pellets are then heated to form a continuous conducting layer intimately bonded to the surface. If there is any absence of internal bonding, the gap between the electrode and the ceramic acts as a series capacitance of low value. The presence of an air gap lowers the effective capacitance of the most ceramic materials. If a field is applied, most of the voltage drop occurs.

Chapter 3

3.1Characterization of LCTO

3.1.1 DSC & TGA

The thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) are methods to investigate the thermal characteristics of substance like polymers and ceramics.

TGA: TGA is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). TGA can gives an information about the physical process, such as second-order phase transitions, which has vaporization, sublimation, absorption, adsorption, and desorption. TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatiles (such as moisture). The sample is heated under nitrogen air and the mass loss is determined during this process.

DSC: DSC is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference pan is measured as a function of temperature. Both the sample and reference pan are maintained at nearly the same temperature throughout the experiment [3,2]

DSC can be used to obtain the thermal critical points like melting points, enthalpy changes, specific heat, glass transition temperature and phase transition temperature of the substances.

3.1.2 X-Ray Diffraction (XRD)

X-ray diffraction analysis investigates different types of phases present in the materials. Crystalline substances act as a three dimensional diffraction gratings for X-ray. Wavelength of X-ray is nearer to the spacing of planes in a lattice. X-ray diffraction is a technique for the study of crystal structures and spacing between the atoms. Principle of X-ray diffraction is constructive interference of monochromatic X-rays from the sample which is crystalline. X-rays are produced by a cathode ray tube, which will produce monochromatic radiation, which is directed toward the sample. The condition satisfy for diffraction is Bragg's Law ($n\lambda=2d \sin\theta$) of diffraction. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystal. The X-rays are detected and then processed and counted. Which is done by scanning the sample through a wide angular range, all possible diffraction peaks are appeared in the pattern. Conversion of the diffraction peaks to d-spacing allows identification of the material because each mineral has a set of unique d- spacing's.

All diffraction methods are based on generation of X-rays in X-ray tube. These X-rays are made to fall at the sample, and the diffracted rays are collected. After calcinations X-Ray diffraction pattern is collected for each sample using powder Diffract meter (PHILIPS, PW 3020) with Cu Kα (1.5405 Å) radiation[3,5]

2.1.6 Scanning Electron Microscopy (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused electron beam. The beam of electrons interact with electrons in the sample, which produces various signals that can be detected and that contain information about the sample's surface topography and composition. The beam of electron is generally scanned by the method of raster scan pattern, and the position of the beam is combined with the detected signal to create an image. SEM has a resolution better than 1 nanometer. Specimens is observed in high vacuum, low vacuum and the environmental SEM specimens can be observed in wet conditions.

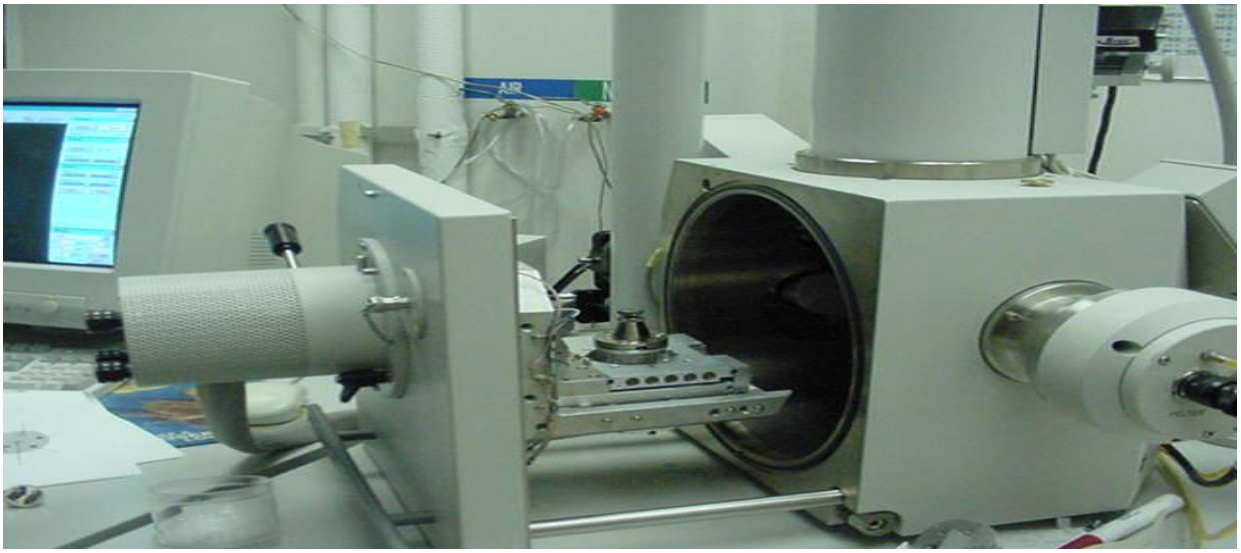


Fig-1 SEM opened sample chamber

The basic principle of SEM involves interaction of the electron beam generated from x ray tube and the sample surface. This interaction generates a variety of signals. These signals includes

secondary electron beam, backscattered electron beam. Backscattered electrons and secondary electrons are used for the imaging of the sample. Secondary electrons are used to study the topography and morphology of the sample whereas the back scattered electrons help to illustrate the contrast in the composition of multiphase samples[4,7]

2.1.7 Dielectric Properties

2.1.7 Dielectric constant and dielectric loss measurement

Ferroelectric ceramics are dielectric whose electrons are bound to the nucleus by strong forces and hence they are not free under the influence of an external field. The molecules may be represented as positive nuclei of charge +q surrounded by a symmetrically distributed negative electron cloud of charge –q. In the absence of an applied field the centers of gravity of the positive and negative charge distributions coincide. When the molecules are placed in an external electric field the positive and negative charges experience electric forces tending to move them apart in the direction of the applied field. The distance moved is very small (10-10m) as the displacement is limited by restoring forces which increases with the increase in displacement. The centers of positive and negative charges no longer coincide and the molecules are said to be polarized. Each molecule now forms a dipole whose moment is defined as $\mu = q\ dx$, where dx is distance between the two centers of the charges and is a vector pointing from the negative to the positive charges. In ferroelectric ceramics a spontaneous polarization can exist even in the absence of an applied electric field. Ferroelectric can thus be used like a capacitor. Giving rise to the polarization of the medium, charges are induced at the surface of the dielectric. Ferroelectric ceramics generally have much higher dielectric constants, typically several hundred to several thousand. It is determined from the calculated capacitance values of the samples using the formula

$$C = (K\varepsilon_O A)/d$$

Where

C: Capacitance

K: dielectric constant

A: area of the electrode

ε_0: permittivity of the free space

When a dielectric material is subjected to an alternating field the orientation of the dipole changes and hence the polarization will tend to reverse every time the polarity of the field changes. As long as the frequency remains low (<100 Hz), the polarization follows the alternations of the field without any significant lag and the permittivity is independent of frequency and has the same magnitude as in a rest field. When the frequency gets increases the dipoles will no longer be able to rotate sufficiently rapidly so that their oscillations will begin to lag behind those of the field. As the frequency is again increased the permanent dipoles, which are present in the medium, will be totally unable to follow the field and the contribution to the static permittivity from this molecular process i.e. orientation polarization ceases. At higher frequencies, usually in the infra-red the relatively heavy positive and negative ions cannot follow the field variation so that the contribution to the permittivity from the atomic or ionic polarization ceases and only the electronic polarization exist for high frequency. The above effects lead to fall in the permittivity of a dielectric material with the frequency. When the applied period voltage is larger than the relaxation time of a polarization process, polarization is essentially complete at any instant during each and every cycle. The current of charging is 90 degree advance in relation to the voltage so that no electrical energy is lost during charging. When the period of the applied voltage is much shorter than the relaxation time for a polarization process, the polarization does not happen at all. Here again, the current of charging is 90 degree

advanced of the applied voltage. When the period is in the same range as the time of relaxation, resonance happens. During resonance, current leads the voltage by (90-δ) where δ is loss angle and tan δ is a measure of the electrical loss because of resonance. The loss due electrical charge at low frequencies is mainly due to dc. resistivity but at high frequencies the electrical loss is mostly due to dipole rotations or due to ionic transitions from the lower state of energy. Due to the upward transition the energy is absorbed from the field applied. The losses which falls under the region of infrared are referred to as infra-red absorption and in the optical region are referred to as optical absorption.

With alternating voltage, the charge stored on a dielectric has both real (in phase) and imaginary (out of phase) components, which is caused by resistive leakage or can be dielectric absorption. The loss is expressed by the ratio of out of phase component to the in phase component. This is the dissipation factor (D) of the dielectric loss, also frequently called loss tangent (tan δ)[3,6].

For the measurement of dielectric constant and dielectric loss were done by electro ding the samples with silver paste. The silver paste coated samples were heated at 500 ^{0}C so as to dry the silver paste on the pellets completely. The dielectric measurements of the sample were done by HIOKI 3532-50 LCR Hi-Tester instrument. The frequency range was taken from 1 kHz to 1 MHz. The dielectric properties were also measured as a function of temperature starting from room temperature.

Chapter 4

3.1 Results and Discussions

3.1.1 DSC and TGA of raw LCTO powder

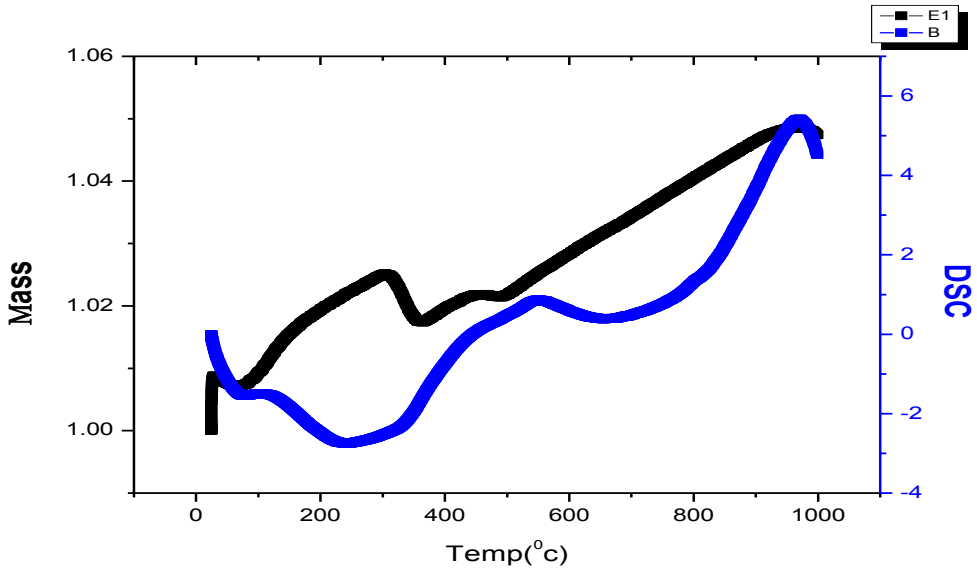


Fig: TGA and DSC curves for the dried modified LCTO Powder

From the TGA graph we find that mass of our sample increases and this is due to the absorption of oxygen at a lowest temperature range there is a sudden fall in mass at temperature 363^0C this is due to evaporation of moisture (H_2O). As the temperature increses the sample eventually reaches its melting temperature the melting process results endothermic peak in DSC curve.

3.1.2 Structure analysis from XRD peaks:

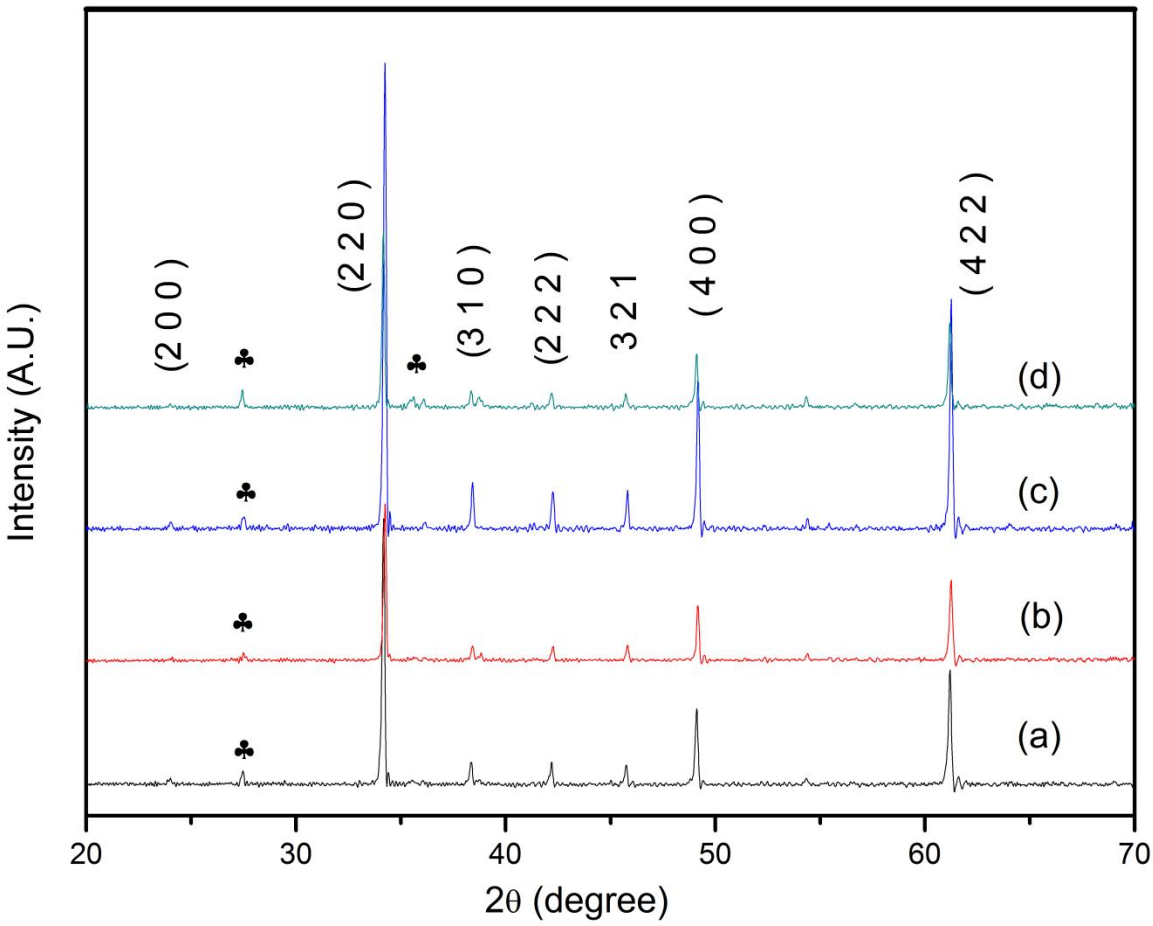


Fig2. XRD pattern of LCTO ceramic calcined at 1000 °C in conventional way for (a) 4 h,(b) 6 h,(c) 8 h, and in microwave for (d) 30 min. ♣ -Unidentified Phase

Indexing performed by using : ICSD -75-2188

Crystal system: Cubic , Space group: Im3

Space group number: 204, a (Å): 7.3910

b (Å): 7.3910, c (Å): 7.3910

Alpha (°): 90.0000 , Beta (°): 90.0000, Gamma (°): 90.0000

The patterns obtained were matched with the reference content in the expert database. The Pattern confirmed the perovskite phase with cubic structure. The XRD diffraction pattern of the sample calcined at 1000 ^{0}C for 4,6 and 8 hours for 30 minutes was taken at an angle of 2θ with a scanning rate of 2^0 per minute with a constant anguler velocity from $(20\text{-}70)^0$.The pattern obtained was matched with the reference content in the expert database. The pattern confirmed the perovskite phase with tetragonal structure. The phase is completely formed at 4 hour calcined sample as we increase the timing of calcination the substance begin to melt that give rise to a secondary peak to the XRD pattern. From that pattern it is cleared that cupper and calcium has diffused to completely into the LCTO lattice to form a solid. LCTO shows a cubic structure.

3.1.2 Scanning electron Microscope (SEM)

The SEM images for samples were taken and their corresponding grain size was calculated using the linear intercept method.

For conventional sintering

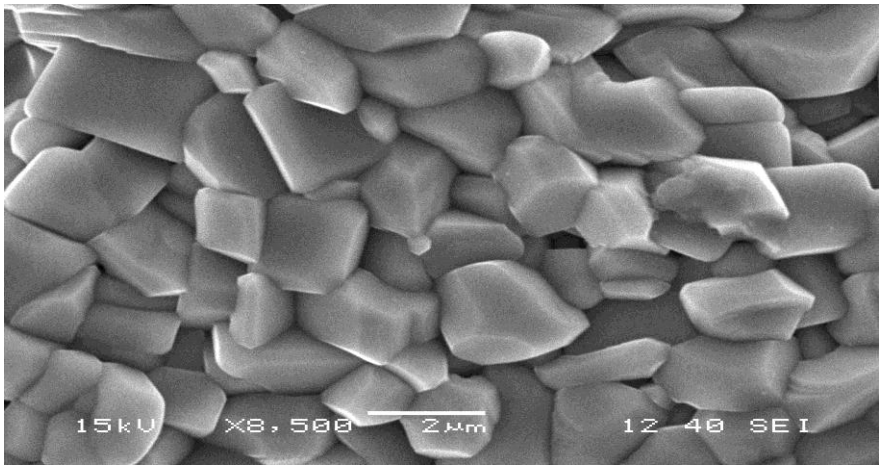


Fig.6 SEM of sample Sintered for 4 hours at 1000^0C

For microwave sintering

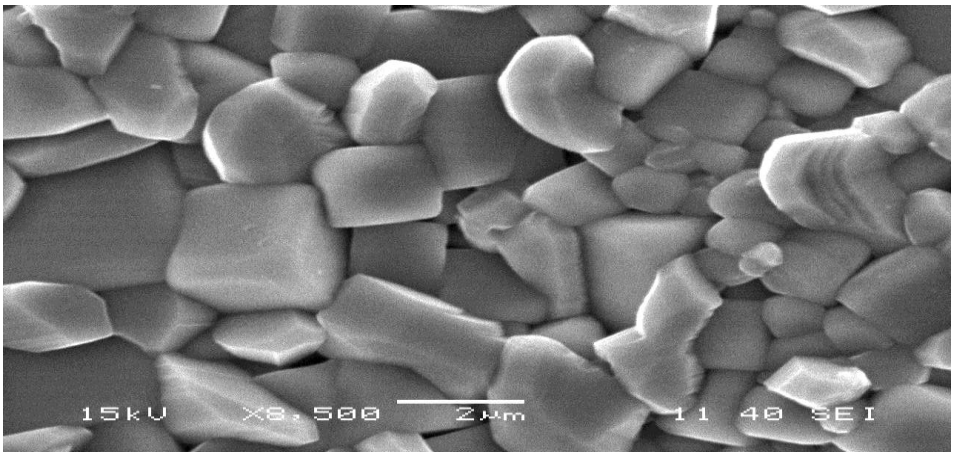


Fig. 7: SEM of sample Sintered for 20 minutes at 1000^0C

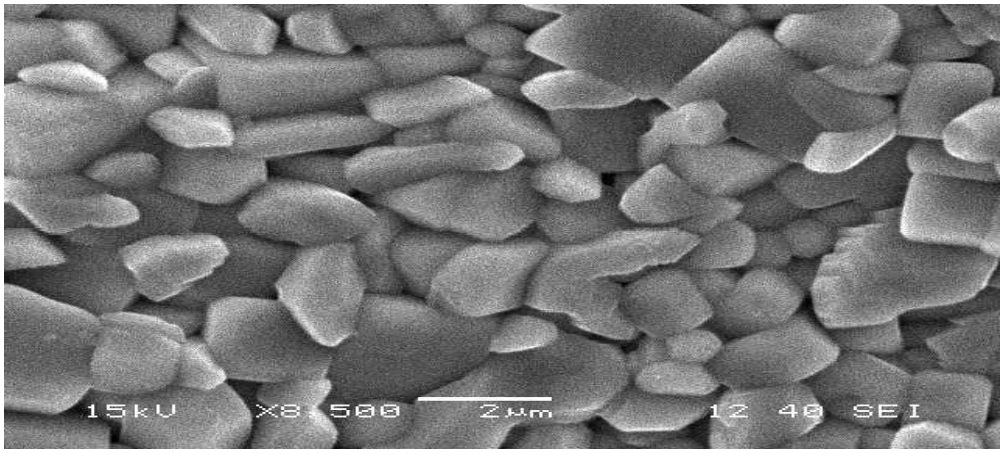


Fig.8: SEM of sample Sintered for 40 minutes at 1000^0C

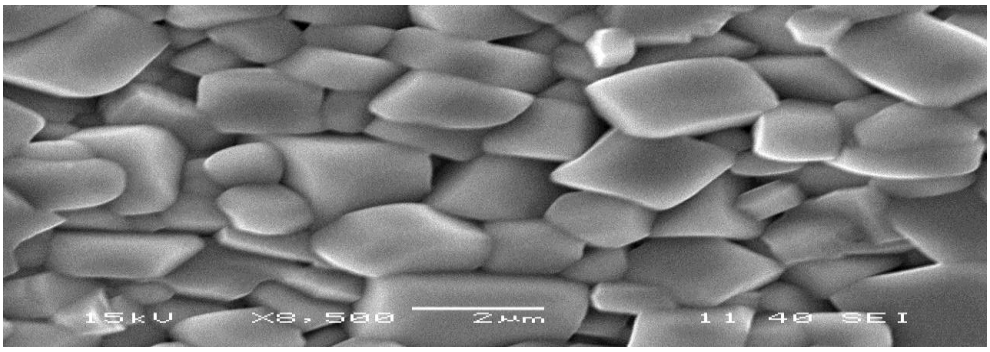


Fig.9: SEM of sample Sintered for 60 minutes at 1000^0C

TABLE FOR CALCULATED GRAIN SIZE:

SAMPLE	CALCULATED GRAIN SIZE
M-60	˜ 2.4µm
M-40	˜ 2.2 µm
M-20	˜1.4 µm
C-4	˜ 1.3 µm

From the above table it is concluded that the grain size of the conventionally sintered samples is less compared to microwave sintered sample. Also the grain size increases in case of microwave sintered sample as we increase the timing of sintering.

3.1.3 Density measurements:

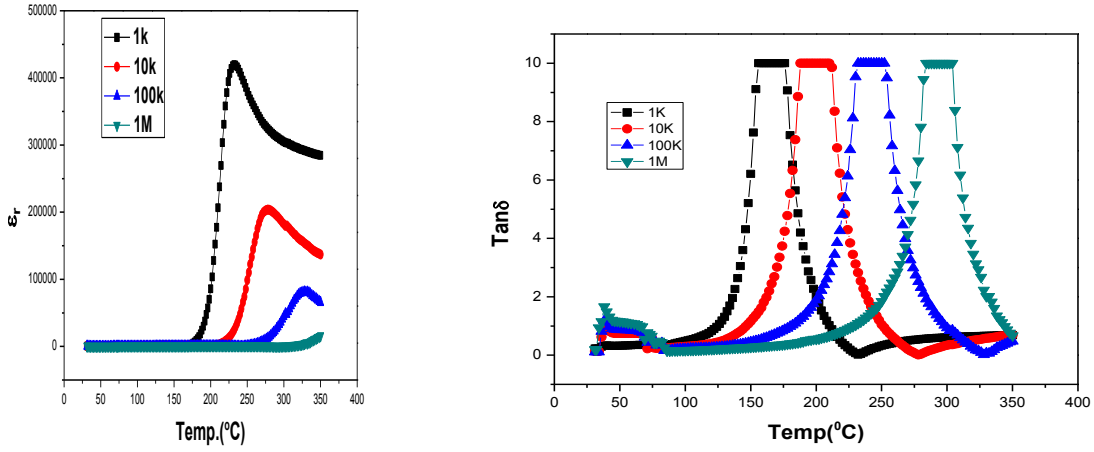
The density was calculated using Archimedes principle for both conventional and microwave sintered samples. The liquid medium taken was water.

SAMPLE	DRY WEIGHT (g)	SUSPENDED WEIGHT(g)	DENSITY IN (g/cm^3)
M-20	0.3596	0.2884	5.05
M-40	0.4146	0.3327	5.06
M-4	0.4709	0.3745	4.88

The highest density of LCTO was obtained to be 5.05 g/cm^3 .The density in microwave sintered method was found to be highest followed by other two samples.

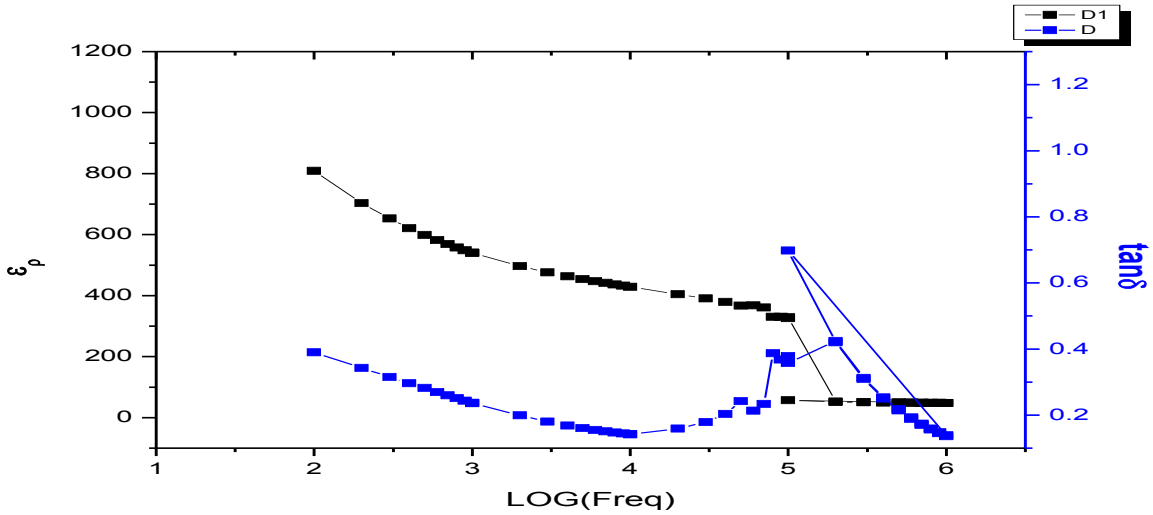
3.1.4 Dielectric measurements:

The figures below show the variation of dielectric constant and dielectric loss with temperature for both microwave and conventional sintered samples.



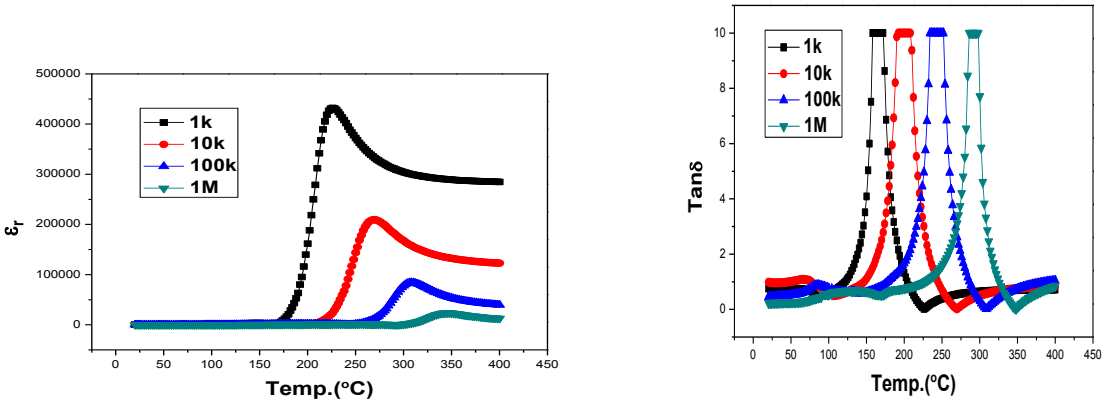
(a) (b)

Fig.10: Variation of (a) dielectric constant and (b) dielectric loss with temperature for MW 20 sample



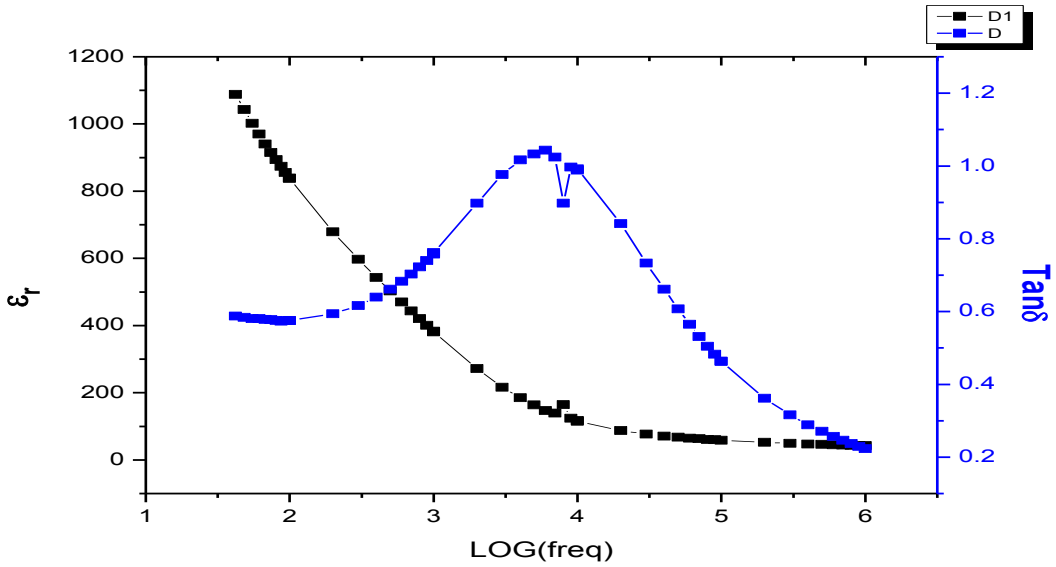
(c)

Fig.11: Variation of dielectric constant and dielectric loss with frequency at room temperature



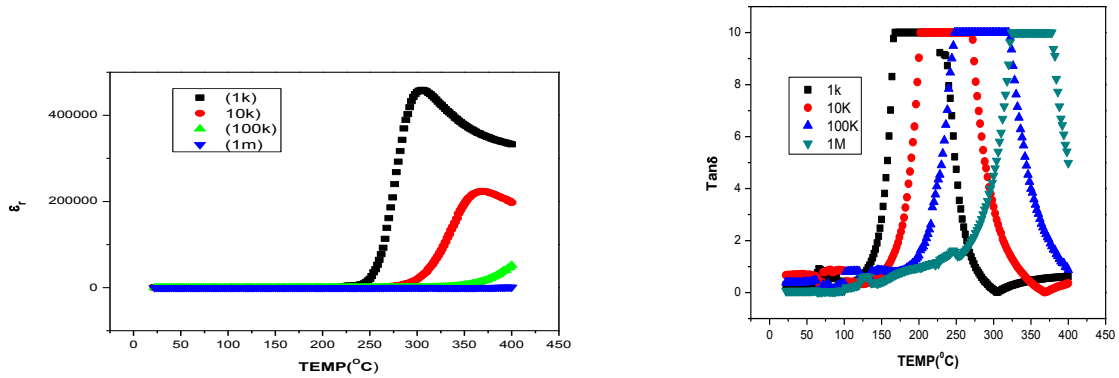
(a) (b)

Fig.12: Variation of (a) dielectric constant and (b) dielectric loss with temperature for MW 40 sample



(c)

Fig.13 Variation of dielectric constant and dielectric loss with frequency at room temperature



(e) **(f)**

Fig.14: Variation of (e) dielectric constant and (f) dielectric loss with temperature for CS 4 sample

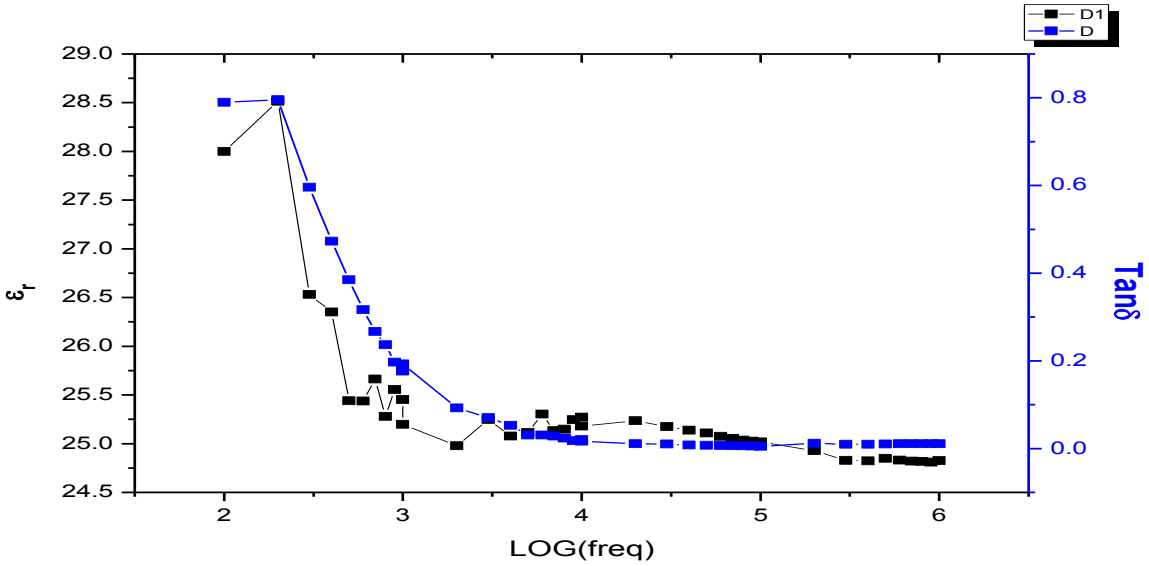


Fig.15: Variation of dielectric constant and dielectric loss with frequency at room temperature

Table 1 Dielectric constant and dielectric loss at 1 kHz frequency

SAMPLE	DIELECTRIC CONSTANT $(\varepsilon_r)_{max}$	DIELECTRIC LOSS $(\tan\delta)_{max}$	(ε_r)DIELECTRIC CONSTANT AT ROOM TEMPRATURE	(Tanδ) DIELECTRIC LOSS AT ROOM TEMPRATURE	DENSITY
M-20	**419858.948**	**9.99**	**540.5168**	**0.23709**	**5.05**
M-40	**428245.13**	**9.99**	**370.0667**	**0.29475**	**5.06**
C-4	**458804.16**	**9.99**	**25.43**	**0.17654**	**4.88**

The value of dielectric constant increases with increase in temperature after a certain value of temperature. The value of dielectric constant remains constant up to a certain temperature, after that it increases suddenly giving rise a peak again decreases to a lower value. The value of dielectric constant increases with increase in temperature up to a certain temperature called the critical temperature after which it starts decreasing with further increase in temperature indicating a phase transition from ferroelectric to Para electric phase. Dielectric constant increases with increase in temperature due to increase in polarization caused because of separation of negative and positive charges at higher temperature.

CONCLUSIONS

It is concluded that he XRD peaks reveal the single phase perovskite with cubic structure. The densities of the sintered sample was measured using Archimedes principle and shows higher density than microwave sintered sample than conventional sintered sample.SEM microstructure shows a dense a dense microstructure in the sample with grain size in the range (1-2)μm. Here from our dielectric constant measurement we find LCTO high value of dielectric constant at room temperature compared to other ceramic.

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